

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Preventing the Formation of and removing Deposits of Solid Paraffins

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to suspending agents suitable for use in the suspending of normally solid paraffinic hydrocarbons in petroleum, and also for preventing the deposition of normally solid hydrocarbons contained in petroleum and to a process for inhibiting the deposition of such normally solid paraffins from petroleum during the production, transportation, or storage of the same.

Petroleum obtained from oil and gas wells will frequently contain normally solid paraffinic hydrocarbons which tend to accumulate in the well bore and in the equipment utilized in producing the petroliferous fluid. In addition, the normally solid paraffins frequently to accumulate in transportation lines, storage vessels and other equipment wherein the petroleum is processed. This presents a serious problem in that the deposition of paraffins interferes with the production, transportation, storage and processing of the petroleum containing such paraffinic materials. Paraffin deposition may proceed to the point where production is completely interrupted.

In the past it has been proposed to overcome this problem through the use of mechanical devices for removing deposited paraffins, through the use of solvents for the paraffins. However, the results that have been obtained have not been entirely satisfactory.

It has now been discovered that fatty acid-amine derivatives as hereinafter defined may be used for the inhibition of the formation of normally solid paraffinic hydrocarbon deposits in or from petroleum, by incorporating in the

petroleum the said fatty acid-amine derivatives. The removal from surfaces of said deposits derived from petroleum may be achieved according to this invention by contacting the deposits with a liquid comprising a solution of the said fatty acid-amine derivative in a hydrocarbon solvent therefor.

The fatty acid-amine derivatives according to this invention are defined as the reaction products prepared by reacting a substantially water-insoluble fatty acid with a primary or secondary amine, the organic radicals attached to the nitrogen of the amine containing not more than two carbon atoms per organic radical, said amine being reacted with fatty acid at a temperature of not more than 200°F. in an amount sufficient to provide an amine salt having the hereinafter described solubility characteristics. The fatty acid derivative may be added to petroleum containing normally solid paraffins in an amount sufficient to prevent deposition of a substantial portion of such paraffins or may be brought into contact with a deposit of normally solid paraffins, in the presence of a hydrocarbon solvent for the fatty acid derivative, in an amount sufficient to suspend the deposited paraffins in the hydrocarbon.

The fatty acids to be used in preparing the derivatives of the present invention are monocarboxylic acids or the dimerized derivatives thereof which are substantially completely insoluble in water. Representative fatty acids which may be used include monocarboxylic fatty acids containing from about 12 to 18 carbon atoms such as lauric acid, tridecanoic acid, myristic acid, palmitic acid, margaric acid, stearic acid, oleic acid, linoleic acid and linolenic acid, and mixtures thereof. The fatty acids may be used in purified form if desired or, preferably, naturally occurring oils containing the same may be used such as, for example, coconut oil, palm oil, tall oil and oiticica oil, and mixtures thereof. Preferred starting materials for the present invention include tall

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oil and also the residue obtained from the production of sebacic acid by the heat degradation of castor oil, such residue primarily containing water-insoluble dimeric fatty acids. A description of this product will be found, for example, in the Cheetham et al United States patent specification No. 2,267,269. The residue is an amber-colored viscous residue containing long-chained carboxylic acids (primarily dimeric fatty acids), such residue having an acid number between about 40 and 200 having an iodine number between 30 and 60, having an average molecular weight of about 1,000, and being the non-volatile material remaining from the vacuum distillation at 270°C. under 4 millimeters Hg pressure of the by-product acids obtained during the preparation of sebacic acid from castor oil.

The amines to be used in accordance with the present invention for reaction with the water-insoluble carboxylic acid are primary and secondary amines having attached, to the nitrogen of the amine, organic radicals containing not more than 2 carbon atoms per organic radical. Representative of the amines of this nature which may be used are monomethyl amine, dimethyl amine, dimethanol amine, monoethyl amine, diethyl amine, monoethanolamine, diethanol amine, ethylene diamine, dimethylenetriamine, diethylenetriamine, triethylenetetraamine and tetraethylenepentamine, and mixtures thereof. A preferred amine which is used with the most satisfactory results is monoethanolamine.

The reaction between the amine and carboxylic acid should be conducted at a temperature of not more than 200°F. and is preferably initiated at room temperature. Heat is normally evolved during the reaction, the rise in temperature normally being such that the temperature at the end of the reaction is about 50°F. higher than the initial reaction temperature. Accordingly, when the reaction is initiated at temperatures above room temperature care should be taken to avoid a rise in temperature during reaction to a temperature in excess of 200° F. This is necessary in that the desired reaction products of the present invention are amine salts which are dehydrated to form amides at temperature above 200°F.

The carboxylic acids are highly viscous or solid materials at room temperatures and, accordingly, the reaction is preferably (although not necessarily) conducted in solvent solution. Any suitable organic solvent may be used for this purpose including, for example, aromatic hydrocarbons such as benzene, toluene, xylenes, and mixtures thereof and chlorinated organic solvents such as carbon tetrachloride, trichloroethane, dichloropentane and dichlorodiethyl-ether, and mixtures thereof. When a solvent is to be used, it is preferable to dissolve the fatty acid in the solvent first and then to add the amine to the thus prepared solution with agitation. It is preferable to use about a 5 to

40 per cent solution of the fatty acid or fatty acid-containing material. The reaction proceeds rapidly and is normally substantially complete on addition of the amine.

Generally speaking, it may be stated that from about 10 to 40 parts of amine should be reacted with about 90 to 60 parts of fatty acid, the amine and fatty acid being reacted in amounts sufficient to provide a reaction product having the hereinafter defined solubility characteristics. For example, when the dimeric fatty acid-containing residue is to be used, about 10 to 25 parts by weight of amine should be reacted with about 90 to 75 parts by weight of residue and, preferably, about 15 to 20 parts of amine are reacted with about 85 to 80 parts of the residue.

As indicated, the amount of amine to be employed will vary with the nature of the fatty acid employed since the fatty acid derivatives of the present invention will have both hydrophobic and hydrophilic properties. The desired reaction products are further defined as those having the following solubility characteristics:

- (a) Water solubility—a 5% solution of the product in pure isopropyl alcohol or mixtures of isopropyl alcohol with up to 45 volume per cent of water is clear and colourless whereas with greater amounts of water the solution is cloudy.
- (b) Oil solubility—a 5% solution of the product in toluene or in mixtures of toluene with up to 45 volume per cent of iso-octane is clear and colourless whereas with greater amounts of iso-octane a cloudy solution is formed.

That is to say, the reaction products of the present invention form a colourless 5% volume solution in a mixture of at least 55 volume per cent of isopropyl alcohol with, correspondingly, not more than 45 volume per cent of water and in a mixture of at least 55 volume per cent of toluene with, correspondingly, not more than 45 volume per cent of iso-octane.

A particularly useful fatty acid-amine derivative is prepared by reacting 15 to 20 parts by weight of monoethanolamine with 85 to 80 parts by weight of the dimeric fatty-acid-containing residue resulting from the distillation of the by-product acids obtained in the preparation of sebacic acid from castor oil.

A thus-prepared fatty acid derivative of the present invention or a mixture of two or more such derivatives is added to a petroleum containing normally solid paraffinic hydrocarbons in an amount sufficient to prevent deposition of a substantial portion of the paraffinic materials. The derivative is preferably added in the form of about a 5 to 40 per cent organic solvent solution. However, if desired the fatty acid derivatives may be added directly to the petroleum without dilution.

The fatty acid-amine derivative may be in-

incorporated in the petroleum as a solution in an organic solvent, which may be for instance a hydrocarbon or chlorinated organic compound.

5 Generally speaking, the amount of derivative to be used will be within the range of about 0.001 to about 10 volume per cent of the petroleum to be treated. In general, satisfactory results are obtained through the use of about 0.001 to about 1 volume per cent.

10 The following examples are given by way of illustration and are not intended as limitations on the scope of this invention.

EXAMPLE I

15 A plurality of fatty acid derivatives were prepared from monoethanolamine. A first group of fatty acid derivatives was prepared by reacting the monoethanolamine with a plurality of samples of tall oil and another group of fatty acid derivatives was prepared by reacting the monoethanolamine in various proportions with a plurality of samples of the dimeric fatty acid-

containing residue described above. The proportions of monoethanolamine to tall oil, and residue comprising dimeric fatty acids are given in Table I. In preparing each of the derivatives, the fatty acid component was dissolved in an amount of xylene sufficient to provide about a 20% solution of the starting material. Next, the desired amount of monoethanolamine was added to the solution with agitation over a period of about 30 minutes. In each instance the reaction was initiated at room temperature and atmospheric pressure. In each instance, a rapid rise in reaction temperature occurred as the monoethanolamine was added, the final reaction temperature being about 140°F. The reactions were substantially complete upon addition of the monoethanolamine. However, the reaction mixtures were held at a temperature of about 140°F for about 30 minutes after addition of the last of monoethanolamine in order to insure completeness of the reaction.

TABLE I—A

Composition of Carboxylic Acid Derivatives

Derivative	Carboxylic Acid Component	Parts by Weight	Amine	Parts by Weight
I	Residue comprising dimeric fatty acids	85	Monoethanolamine	15
II	Residue comprising dimeric fatty acids	80	Monoethanolamine	20
III	Residue comprising dimeric fatty acids	70	Monoethanolamine	30
IV	Tall Oil	80	Monoethanolamine	20
V	Tall Oil	70	Monoethanolamine	30
VI	Tall Oil	60	Monoethanolamine	40
VII	Tall Oil	40	Monoethanolamine	60

TABLE I—B

Solubility of Carboxylic Acid Derivatives

Derivative	Water Solubility (Clear 5 Vol. % Solution in a Mixture of 55 Vol. % Isopropyl Alcohol with 45 Vol. % of water)	Oil Solubility (Clear 5 Vol. % Solution in a Mixture of 55 Vol. % Toluene with 45 Vol. % of Iso-octane)
I	Soluble	Soluble
II	Soluble	Soluble (Slightly Hazy)
III	Soluble	Insoluble
IV	Soluble	Soluble
V	Soluble	Soluble
VI	Soluble	Soluble
VII	Soluble	Insoluble

EXAMPLE II

5 The xylene solutions of the fatty acid derivatives prepared in Example I were tested to determine their effectiveness as paraffin suspending agents. The test employed was as follows.

10 A sample of a highly paraffinic crude oil from the Luling Field was centrifuged, and it was found that about 50 volume per cent of the material in the crude oil sample could be separated by centrifugation. It was found that the separable solids material consisted of about 95 volume per cent of paraffinic hydrocarbons and about 5 volume per cent of other separable materials (primarily a water-oil emulsion). In conducting the tests, a given volume of a xylene solution of one of the derivatives of Example

I was added to a portion of the crude oil sample and the resultant mixture was agitated. 20 Thereafter, the resultant solution was centrifuged in order to separate solid materials which were not suspended by the fatty acid derivative. The results are set forth in Table II. It is to be noted from Table II that the results 25 obtained are expressed both in terms of the percentage of separable solid materials suspended and also in terms of the percentage of paraffin suspended. This has been done in order to emphasize that it is the paraffinic hydrocarbons which are suspended in accordance 30 with the present invention and not other types of separable solids such as oil and water emulsions.

TABLE II

Run No.	Derivative	Vol. % of Derivative Added*	% Separable Solids Suspended	% Paraffin Suspended
1	I	10	84	93
2	I	12.5	92	96
3	I	15	94	98
4	II	10	38	40
5	II	12.5	94	98
6	II	15	96	100
7	III	10	0	0
8	III	12.5	16	17
9	III	15	26	27
10	IV	10	0	0
11	IV	12.5	27	28
12	IV	15	59	61
13	V	10	84	93
14	V	12.5	92	96
15	V	15	94	98
16	VI	10	12	12
17	VI	12.5	45	47
18	VI	15	74	77
19	VII	10	0	0
20	VII	12.5	11	11
21	VII	15	11	11

* Derivative added as a 20% xylenes solution

From Table II it will be noted that the results which were obtained were not uniform. Derivatives I to III prepared by reacting monoethanolamine with the residue comprising dimeric fatty acids were tested in runs 1 to 9. Runs 1 to 3 show that derivative I was an effective suspending agent which gives excellent results and that derivative II was an effective suspending agent at the higher concentrations (runs 5 and 6) but not at the lowest concentration (run 4). Runs 7 to 9 show that derivative III was not particularly effective as a suspending agent.

Runs 10 to 21 show the results obtained with respect to derivatives IV to VII obtained by reacting monoethanolamine with tall oil. Runs 10 to 12 show that derivative IV was only partially effective as a suspending agent at the highest concentration (run 12). From runs 13 to 15 it is seen that derivative V was an effective paraffin suspending agent giving excellent results. Runs 16 to 18 show that derivative VI gave satisfactory results at the highest concentration (run 18). Derivative VII was not an effective paraffin suspending agent as shown by the results obtained in runs 19

to 21.

Equivalent results are obtained when about 85 parts of the dimeric fatty acid-containing residue are reacted with about 15 parts of ethylene diamine or with about 15 parts of diethylene triamine in solvent solution at room temperature to give derivatives which are tested in the above described manner.

EXAMPLE III

As another example, about 8.5 liters of high paraffin content crude petroleum were circulated through a $\frac{1}{2}$ " internal diameter galvanized pipe cooled to a temperature of about 80°F. for about 96 hours. At the end of this time the pipe was weighed to determine the amount of paraffin deposited therein and was then cleaned. It was found that about 35.5 milligrams of paraffin per inch of pipe per hour had been deposited during the run. Thereafter, about 1 volume per cent of derivative V (Table I) was added to the crude oil as a 20 per cent xylenes solution and the test procedure was repeated. It was found that in this instance the rate of deposition was only about 9.5 milligrams per inch of pipe per hour.

The same results were obtained through the use of about 1 volume per cent of derivative I.

EXAMPLE IV

A 500 barrel tank of crude oil was found to have a bottom deposit of about 9 inches of paraffin. About 1 gallon (i.e., about 0.005 volume per cent) of a 20% xylenes solution of derivative I (Table I) was added to the storage tank and thereafter the bottom of the storage tank was rolled (i.e., vigorously agitated) in order to agitate the deposited paraffins. The rolling lasted for about one-half hour. At the end of 1 day it was found that the deposited material amounted to less than 3 inches and was of a substantially non-paraffinic nature (i.e. consisted of emulsion, scale and impurities).

In another instance, one gallon of a 20% xylenes solution of derivative I (Example I) was added to a 500 barrel storage tank having about a 20 inch deposit of paraffin on the bottom thereof. The tank was rolled for about one-half hour. At the end of about 1 day only about 9 inches of material had again settled to the bottom of the tank, such material again being of a substantially non-paraffinic nature.

WHAT WE CLAIM IS:—

1. A fatty acid amine derivative which is the reaction product of a substantially water-insoluble fatty acid with a primary or secondary

amine having attached to the nitrogen of the amine organic radicals containing not more than 2 carbon atoms per radical, said amine being reacted with said fatty acid at a temperature not more than 200°F in an amount sufficient to provide a reaction product forming a colourless 5 volumes per cent solution in (a) mixtures of at least 55 volume per cent of isopropyl alcohol with water and (b) mixtures of at least 55 volume per cent of toluene with isooctane.

2. A method for inhibiting the formation of normally solid paraffins in or from petroleum, which comprises incorporating a fatty acid amine derivative as claimed in claim 1 into the petroleum.

3. A method as in claim 2 wherein the said fatty acid amine derivative is added to said petroleum as a solution in an organic solvent.

4. A method for suspending or removing from surfaces, deposits of normally solid paraffins, which comprises contacting the deposits with a liquid comprising a solution of the fatty acid amine derivative as claimed in claim 1 in a hydrocarbon solvent therefor.

5. A method as in claim 3 or claim 4 wherein the solvent is an aromatic hydrocarbon.

6. A method as in claim 3 wherein the solvent is a chlorinated organic compound.

7. A method as in any of claims 2 to 6 wherein the amine is monoethanolamine.

8. A method according to claim 7 in which said fatty acid amine derivative is prepared by reacting about 25 to about 30 parts by weight of monoethanolamine with about 75 to 70 parts by weight of tall oil in solution in a non-reactive organic solvent.

9. A method according to claim 7 in which said fatty acid amine derivative is prepared by reacting 15 to 20 parts by weight of monoethanolamine with 85 to 80 parts by weight of the dimeric fatty acid-containing residue resulting from the distillation of the by-product acids obtained in the preparation of sebacic acid from castor oil.

10. A method according to claim 2 in which said fatty acid derivative is incorporated in petroleum in proportions of from 0.001 to 10 volume per cent, based on the petroleum.

11. The method according to claim 2 or claim 4 substantially as hereinbefore described with reference to the examples.

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